Crucible Materials Corporation

Corrosion-Resistant Steel Through Powder Metallurgy Process

In the 1990s, intergranular stress corrosion cracking in alloys was a growing problem in the United States. In this type of corrosion, cracking occurs along the grain boundaries (anomalies, or uneven portions) of an alloy when it is both under stress and in a corrosive environment, such as salt water. While the need to utilize the earth's oceans for fuel, minerals, energy, and food was increasing, the ability to effectively use this natural resource would require materials that were more resistant to salt water corrosion and less expensive than those currently available. The only alloys that demonstrated resistance to corrosion in seawater were expensive and often difficult to weld or fabricate.

Crucible Compaction Metals, a powder metallurgy production facility and division of Crucible Materials Corporation, estimated that the annual economic loss from corrosion was approximately $80 million. This included preventative actions, replacement and loss of products, and safety and product liability issues. To limit these huge economic losses, the company proposed to use a new design methodology to manufacture high-strength, high-nitrogen stainless steel that had superior intergranular stress corrosion cracking resistance in seawater and other high-chloride environments. In 1995, the company was awarded cost-shared funding from the Advanced Technology Program (ATP) to develop new alloys for stainless steel using the company's proposed process.

By the end of the three-year ATP-funded project in 1998, Crucible had developed high-nitrogen alloys that could improve the performance of stainless steel and had identified potential commercial applications for one stainless steel, SS100. Due to the cost of developing and marketing SS100, the company decided not to commercialize it at that time. Crucible is interested in developing and commercializing SS100 in the future and has continued to consider different markets for it, including the boat shaft and medical implant markets.

COMPOSITE PERFORMANCE SCORE
(based on a four star rating)
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Crucible Proposes Improved Powder Metallurgy Process

In the 1970s, steel manufacturers were adding up to 0.12 percent nitrogen to improve the strength and corrosion resistance of stainless steel. Since then, alloys with nitrogen contents as high as 0.5 percent have been produced, further increasing corrosion resistance and strength. However, as increasing amounts of nitrogen are added to an alloy, the molten components cool and segregate into different phases (crystal structures), making it difficult to shape the alloy.

In the mid-1990s, Crucible Materials Corporation created a mathematical model to predict the corrosion resistance of steel alloys. This model predicted that increasing the nitrogen content should lead to superior corrosion resistance. Crucible proposed to develop a powder metallurgy process, using inert gas atomization to produce powder particles, followed by rapid solidification to achieve the desired homogeneous chemistry. In this process, powder is created by impinging high-pressure gas onto a molten metal stream to disintegrate the metal into drops that rapidly form solid spheres upon cooling. Crucible believed that the powder metallurgy process, which had already been successfully used to produce segregation-free high-alloy tool steel with no workability problems, could also be applied to the development of an alloy for high-strength, high-nitrogen stainless steels.

Mathematical Model Used to Predict Experimental Alloys

Crucible's goal was to use both its mathematical model, based on thermodynamic data from recent literature, and rapid solidification technology to manufacture high-strength, high-nitrogen stainless steel that is resistant to intergranular stress corrosion cracking in seawater and high-chloride environments. To accomplish this, the company planned to use its mathematical model to create a matrix of high-nitrogen, iron-based alloys that were predicted to have high corrosion resistance. Crucible would melt and atomize 50 pounds each of 10 different experimental alloys to produce powder and use heat and high pressure to isostatically press the powders into test blocks. Each test block would be chemically analyzed, thermally processed, and tested for strength and corrosion resistance.

The results of this experiment would check the predictions of the model, and the alloy with the most promise would be atomized in an 800-pound unit to produce powder that would be extensively tested to verify the laboratory results taken from the 50-pound sample. A finished product, a near-net-shape part, would then be manufactured and sent to an end user for a field application and trial.

Crucible's goal was to use both its mathematical model and rapid solidification technology to manufacture high-strength, high-nitrogen stainless steel.

Crucible believed that, if successful, this development would reduce the United States' corrosion-related losses by $80 million each year. However, there was a significant technical risk involved in undertaking the project. At the time, powder metallurgy was not performed according to a scientific model. In addition, Crucible anticipated difficulty in creating a component with enough solubility to absorb and retain sufficient nitrogen. Furthermore, the development effort would be costly and would require an extended length of time to complete. Because of the technical risk and cost factors, the company was unable to proceed without outside funding. Therefore, in 1994, Crucible applied for cost-shared funding from ATP and was awarded $908,000 for a three-year project that began in March 1995.

Reduced Corrosion Losses Could Lead to Broad-Based Benefits

The new high-strength, high-nitrogen stainless steel could potentially benefit a broad section of American industry by limiting the huge economic losses caused by corrosion. If successful, this development project would also reduce the need for expensive alloys; result in new methods and processes that could be applied to existing technologies; create new markets for high-strength, corrosion-resistant products; and enhance U.S. competition in overseas markets.

In 1994, the total annual consumption of stainless and heat-resistant steels in the United States was approximately 1.5 million tons. One significant production cost factor was the need to use expensive metals such as chromium, nickel, and molybdenum. Crucible anticipated that if 10 percent of the chromium and nickel in these alloys was replaced with low-cost nitrogen, a yearly cost savings of nearly $150 million in strategic metals could be realized. Strategic metals, such as chromium and nickel, are expensive, are imported, and have limited availability. If 10 percent of the molybdenum could be replaced with nitrogen, another $30 million could be saved. Existing highly alloyed nickel-based materials were resistant to corrosion, but had only moderate strength and were very expensive. They were used only for essential, strategic components.

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Methods developed during the ATP-funded project to maximize the nitrogen content in stainless steels would represent a significant advance in metals processing. In addition, the technology could be applicable to other processes for improving corrosion resistance, such as surface treatment of stainless steels. The technology developed during this project could also be applied to increase nitrogen levels in other important alloys such as nickel-based superalloys.

Manufacturers of valves and other products, in which stress corrosion is an ongoing problem, would significantly benefit from the more corrosion-resistant and stronger stainless steel. In addition, the ability to produce both advanced alloys and near-net shapes via powder metallurgy would help domestic producers compete overseas.

Project's Technical Objectives Are Established

Crucible's goal was to develop and commercialize a more corrosion-resistant stainless steel. To meet this goal, the company established the following technical objectives:

- Apply existing thermodynamic models of melt composition and nitrogen pressure for alloys in order to design corrosion-resistant, high-strength, high-nitrogen stainless steel
- Develop the commercially viable powder metallurgy process to obtain unusually high nitrogen compositions
- Develop commercial-scale processing methods to minimize nitrogen loss during subsequent thermomechanical processing of powdered metals
- Study the microstructure of the powder, formed parts, and specimens exposed to high temperatures through the use of optical microscopy, x-ray diffraction, scanning electron microscopy, and transmission electron microscopy
- Evaluate the mechanical properties, corrosion resistance, weldability, and machinability of the formed parts

High-Nitrogen Alloys Are Developed but Not Commercialized

During the ATP-funded project, Crucible developed several alloy compositions that could potentially be used to improve the performance of stainless steel. The company also identified a number of potential commercial opportunities for one stainless steel, SS100. This included applications for Norfolk Southern Corporation, which had tested the material as a candidate for railroad applications, and for Cameron Oil Tool, Dupont, and Westinghouse, to which Crucible had sent material for testing.

The company determined, however, that it was unable to assume the cost of developing and marketing SS100 at that time. Although Crucible was prepared to manufacture the material by using its powder metallurgy process, the company lacked the equipment needed to shape the material into the intended applications. This meant that Crucible would have to complete the process by relying on services outside the company. Crucible had also experienced some difficulties in developing SS100 (as well as the other alloys), such as maintaining a high level of nitrogen while melting and atomizing the composition, which would have added to the production cost.

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In spite of the difficulties, though, Crucible believed that the work it performed in the ATP-funded project was important, and the company continued to fund the development of high-nitrogen alloys after the project ended. Crucible developed one patent as a result of its research and published several articles to explain the research to other engineers.

Conclusion

With ATP's assistance, Crucible developed several high-nitrogen alloys that may be used to produce high-strength, corrosion-resistant steel, and the company identified several potential commercial opportunities for one stainless steel, SS100. Due to the high cost of developing and marketing SS100, the company decided against commercializing it when the ATP-funded project ended. Crucible is interested in commercializing SS100 in the future and has continued to consider potential markets for it, including the boat shaft and medical implant (for example, hip or knee) markets. During the project, Crucible received one patent and published several articles describing its advances in developing the high-nitrogen alloys.

PROJECT HIGHLIGHTS
Crucible Materials Corporation

Project Title: Corrosion-Resistant Steel Through Powder Metallurgy Process (Rapid Solidification Powder Metallurgy for High-Nitrogen Stainless Steels)

Project: To develop new corrosion-resistant steels for marine and other corrosive environments using rapid solidification powder metallurgy for high-nitrogen stainless steels.

Duration: 3/15/1995-3/14/1998
ATP Number: 94-01-0287

Funding (in thousands):

ATP Final Cost	$ 908	56%
Participant Final Cost	721	44%
Total	$1,629	

Accomplishments: Crucible Materials Corporation developed several alloys with high levels of nitrogen that demonstrated the potential to produce high-strength, corrosion-resistant stainless steel. These high-nitrogen alloys may be used in stainless-steel products and marketed in the future.

Crucible was granted the following patent:

- "High strength, corrosion resistant austenitic stainless steel and consolidated article" (No. 5,841,046: filed May 30, 1996, granted November 24, 1998)

Commercialization Status: Crucible has not yet commercialized stainless-steel products made from the high-nitrogen alloys developed during this ATP-funded project.

Outlook: At this time, Crucible plans to develop and market one stainless steel, SS100, in the future. It is considering various markets for SS100, including the boat shaft and medical implant markets.

Composite Performance Score: * *

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Publications and Presentations:
Since 1995, Crucible has published or presented the following papers:

- Rhodes, Geoffrey O. and John J. Conway. "High-Nitrogen Austenitic Stainless Steels with High Strength and Corrosion Resistance." JOM. Vol. 48, No. 4, pp. 28-31. April 1996.
- Rhodes, Geoffrey O., John J. Eckenrod, and Frank J. Rizzo. "High Nitrogen Corrosion Resistant Austenitic Stainless Steels Made by Hot Isostatic Compaction of Gas Atomized Powder." Corrosion 96, The NACE International Annual Conference and Exposition. Paper No. 416. 1996.
- Rhodes, Geoffrey O., Ulrike Habel, John J. Eckenrod, and John J. Conway. "Development, Properties and Applications of High Strength Corrosion Resistant High-Nitrogen Austenitic Stainless Steels Produced by HIP P/M." Advanced Particulate Materials & Processes 1997. Proceedings of the 5th International Conference on Advanced Particulate Materials & Processes. 1997.
- Rhodes, G.O. and W.B. Eisen. "High Nitrogen Corrosion Resistant Austenitic Stainless Steels Produced by HIP P/M Processing." Materials Science Forum. Vols. 318-320, pp. 635-648. 1999.

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